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The Microscopic Basis of the Low-Frequency Excitations in B_2O_3 Glass

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We have performed ab initio molecular orbital calculations on the clusters modeling the medium-range ordering (MRO) region of B_2O_3 glass at the Hartree-Fock (HF)/6-31G* levels. Their equilibrium geometries, harmonic vibrational frequencies, and Raman scattering intensities have been calculated. The calculations have reproduced the boson peak frequencies of vitreous B_2O_3 observed at 24 cm^{-1} and 137 cm^{-1}. The normal coordinates have demonstrated that these low-frequency vibrational modes are due to the wavelike motions of atoms within the region composed of one (for the mode at 137 cm^{-1}) or two (for the mode at 24 cm^{-1}) boroxol ring(s). The results suggest that the boson peak originates from the collective harmonic vibrations localized in the MRO region of glasses.

Keywords: *B_2O_3 glass*, Raman spectra, Low-frequency properties, Molecular orbital calculations, Localized vibrations

The low-frequency (< 200 cm^{-1}) relaxations and vibrations in amorphous systems have been the focus of numerous studies aimed at understanding the anomalous low temperature properties and glass transition phenomena observed in such systems. Although the relaxational part of the dynamics in supercooled liquids is well described by the mode coupling theory (MCT) [1], the vibrational excitations generally called the "boson peak" cannot be explained with MCT, and the origin of the boson peak is still unsettled. Thus, the understanding of the boson peak near the glass transition temperature T_g remains an important goal in solid-state physics today. It has recently been suggested that the atomic motions in a medium range scale of the order of ~10 Å in amorphous solids have a close relation to the boson peak [2]. This strongly suggests that the normal-mode analysis of molecules modeling a medium range order (MRO) in a particular glass will shed new light on the physical origin of the boson peak.

B_2O_3 glass has been widely used to study its low-frequency vibrational properties [3]. The low-frequency Raman scattering spectra of B_2O_3 glass are characterized by a nonsymmetric boson peak with a broad maximum around 25 cm^{-1}; the peak shifts slightly to higher frequencies with decreasing temperature. In this work, ab initio molecular

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Scope of research

Inorganic amorphous materials with various functions are the targets of research in this laboratory. (1) To obtain a clear view of "what is glass" and the bases for designing functional glasses, we investigate the structure of glasses using X-ray and neutron diffraction analysis, high resolution MAS-NMR, and ab initio MO calculation. (2) To develop materials of high optical nonlinearity, we search heavy metal oxide-based glasses and transition metal oxide thin films, and evaluate the nonlinear optical properties by THG and Z-scan methods. (3) Using sol-gel method, synthesis and microstructure control are carried out on ceramic/metal/organic dye composite thin films.

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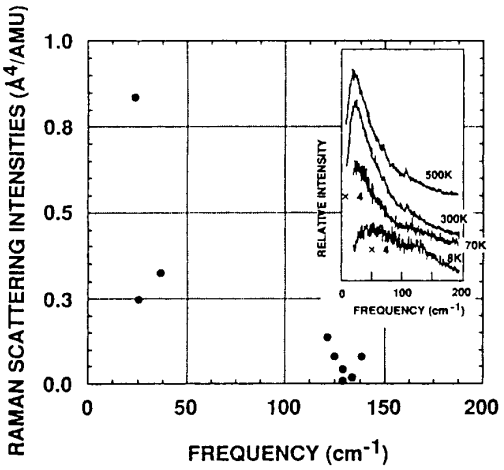

Figure 1. Calculated Raman scattering intensities at the HF/6-31G* level. Inset shows the observed Raman spectra of B_2O_3 glass (Ref.3).

orbital (MO) calculations were carried out to investigate the low-frequency vibrational properties of B_2O_3 glass [4]. It has previously been shown that ab initio MO calculations are useful to investigate the electronic and vibrational properties of glasses [5-7]. We employed the optimized $B_3O_3(OH)_2$-O-$B_3O_3(OH)_2$ cluster as a model of MRO in vitreous B_2O_3. The hydrogen atoms in the cluster are used to saturate the dangling bonds of "surface" oxygen atoms. The $B_3O_3(OH)_2$-O-$B_3O_3(OH)_2$ cluster is composed of two boroxol rings; the boroxol rings are considered to be the principal structural units in B_2O_3 glass. All ab initio MO calculations were carried out using the GAUSSIAN92 computer program [8] on CRAY Y-MP2E/264 super computer in this Institute.

We notice from Fig.1 that the low-frequency vibrational modes for the model cluster can be separated into two regions. One lies from 23 cm^{-1} to 37 cm^{-1} (group I) and the other from 121 cm^{-1} to 138 cm^{-1} (group II). Figure 1 also compares the calculated results with the observed Raman spectra [3]. It should be noted that the two vibrational regions satisfactorily correspond to the observed frequencies (24 and 137 cm^{-1}) of the two boson peaks of B_2O_3 glass at room temperature.

We next analyze the normal coordinates to investigate what kinds of motion yield the low-frequency vibrational modes. Figure 3 depicts the normal coordinates of the vibrational modes calculated at the 6-31G* level. All these vibrational modes exhibit a sort of out-of-plane bending motions of the whole skeleton of the cluster. We refer to these low-frequency vibrational motions as the "wavelike" motions because they can be regarded as swelling motions to form "waves" having specific "wavelengths." It appears from Fig. 2 that the "wavelength" becomes shorter with increasing frequency of the modes. For the modes in group I (see, for example, Fig.2 (a)) the "wavelengths" are the extent of the two boroxol rings (~ 10 Å), while for the modes in group II (see, for example, Fig.2 (b)) they are the extent of one boroxol ring or that of one O-B-O-B bond. Thus we suggest that the boson peak results from the harmonic vibrational motions localized in the extent of the medium-range order (MRO) in the respective glass-forming systems.

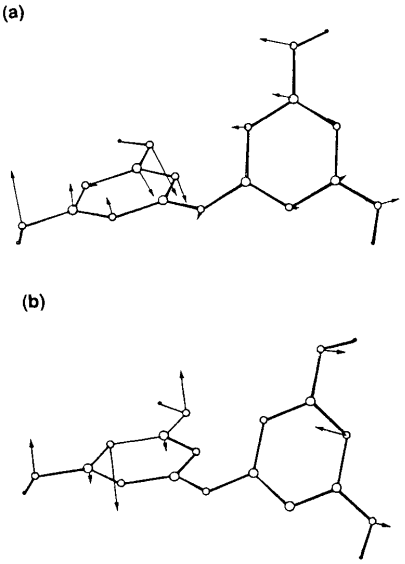

Figure 2. Calculated normal-mode coordinates for the modes at (a) 24 cm^{-1}, and (b) 129 cm^{-1}.

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